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Letter of Guest Editor

Remark on the paper of J.-U. Sommer and G. Reiter and the "discussion of problems" by B. Wunderlich

It is a long tradition that the Lähnwitz Seminar serves as a platform for intensive and frank discussions therefore the editors are of the opinion that the respective special issue of *Thermochimica Acta* should mirror this spirit as well. The paper of J.-U. Sommer and the comments of B. Wunderlich seem in the first moment to be very contradictory and the reader may think that only one position can be the right one. However, true or not the editors agree that the spirit of the Lähnwitz seminar warrant to publish the papers together. To avoid unnecessary misunderstandings, we want to make some annotations in what follows. The knowledge of all referee comments was, of course, very helpful for the editors in this context and should be acknowledged here.

Firstly, it should be mentioned that J.-U. Sommer and G. Reiter are physicists, whereas B. Wunderlich is a chemist and, in addition, that they belong to different generations. Their education in thermodynamics is hardly comparable. The chemists, at least the students in Germany in the middle of the last century, were intensively taught classical thermodynamics on the basis of Max Planck's famous book from 1897. The students of physics on the other hand, in particular the younger generation, have rarely heard lectures on this classical topic. They are mainly taught a thermodynamics which is founded on "modern" statistical physics.

Secondly, it should be pointed out that chemist prefer to think in macroscopic expressions (like phases and states) to describe and model bulk properties of materials, whereas physicists prefer microscopic models on atomic or molecular scales to describe matter properties quantitatively. These are rather different "languages", which often gives rise to misunderstanding and as a result to disagreement.

Having these facts in mind, the above-mentioned point at issue becomes minor important and the discrepancies between the two papers wane. In other words, the paper of Sommer and Reiter is, as far as the thermodynamics is concerned, written in a "dialect", which physicists prefer (may be somewhat too sloppy), whereas the paper of Wunderlich is written in classical and precise style of a past master. The guest editor and the referees agree that both papers are right and should be published. To position them together with this letter in the special issue may help to clarify possible misunderstandings.

Another point, likewise mentioned by one of the referees, may be helpful in this context: in classical thermodynamics, the "particles" (the statistical element) were assumed point like and numerous and the phase very large compared to the size of a single particle. This is needed for the system to be homogeneous in equilibrium with constant variables and negligible fluctuations in space and time. Small molecules, in particular gases and organic or inorganic liquids, meet this premise without problems, but in the case of macromolecules things get very difficult. There are different possibilities to define the statistical element (the particle). It can be the whole macromolecule (e.g. in the case of very diluted solutions) or the repeat unit (e.g. the CH_2-group in the case of poly-olefins) or multiples of the latter (e.g. 2 or 3 repeat units forming a certain "conformation") or even longer parts of the chain (e.g. the all-trans part, the "stem" in lamella crystals). It is clear that these different statistical elements give rise to different models and therefore also different thermodynamics, at least within statistical physics.

In the case of small polymer systems or thin films, it may happen that one single molecule forms the complete phase (a single-molecule liquid or a single-molecule crystal). It is clear that such a single-particle system is in contradiction to the above-mentioned premise for classical thermodynamics and that equilibrium thermodynamics in the sense of constant variables, i.e. homogeneity and negligible fluctuations, cannot be assumed anymore. The tools of classical thermodynamics meet their limits and microscopic or statistical models, like that of Sommer and Reiter, have to be used. Of course, the referee is right when he states that the thermodynamic argumentation of these authors in Section I of their paper is not needed for their model and could easily be misunderstood in this context. However, the paper of Wunderlich may

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contribute to clarify the situation and has therefore been published as well.

Hopefully, this letter could contribute its share toward better intelligibility of the different "languages" of the authors and therefore help to avoid possible misunderstanding of these papers and help the reader to see the issue.

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